CHAPTER 3

EPA/NSF ETV
EQUIPMENT VERIFICATION TESTING PLAN FOR
REMOVAL OF VOLATILE ORGANIC CHEMICALS (VOCs)
BY ADSORPTIVE MEDIA

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1.0   INTRODUCTION AND BACKGROUND

1.1   Introduction

This document is the NSF International (NSF) Equipment Verification Testing Plan for volatile organic chemical (VOC) removal by adsorptive media used in packaged and/or modular drinking water systems for small public or private water supplies. This Testing Plan is to be used as a guide in the development of a Field Operations Document (FOD) for testing adsorptive media treatment equipment within the structure provided by the NSF Protocol Document for VOC removal. Refer to *Protocol for Equipment Verification Testing for VOC Removal* for further information.

This document is applicable only to fixed-bed adsorption processes in which adsorption occurs as water flows through a stationary bed of adsorptive media. It is anticipated that most such systems will use granular activated carbon (GAC) as the adsorptive media, but other media types are also acceptable for verification testing. **This document is NOT applicable to systems using powdered activated carbon (PAC) or other diffuse adsorption processes in which the adsorptive media are added directly to water.**

Standard pretreatment, such as cartridge filtration, included as part of the packaged/modular adsorption treatment equipment is considered an integral part of the treatment system. In such cases, the system shall be considered as a single unit and the pretreatment process shall not be separated for evaluation purposes.

Additional pretreatment processes which may be required to reduce particle loading to the adsorption process for surface water applications are considered to constitute a separate treatment module whose performance and operation are outside the scope of this document. Where such pretreatment is required to reduce the fouling potential of the adsorption process feed water, consult the NSF document *Protocol for Physical Removal of Microbiological and Particulate Contaminants* for evaluation testing procedures.

In order to participate in the equipment verification process for adsorption processes, the equipment Manufacturer shall retain an NSF-qualified Field Testing Organization (FTO) to employ the procedures and methods described in this test plan and in the referenced NSF Protocol Document as guidelines for the development of the FOD. The FOD should generally follow those tasks outlined herein, with changes and modifications made for adaptations to specific equipment. At a minimum, the format of the procedures written for each Task should consist of the following sections:

- Introduction
- Objectives
- Work Plan
- Analytical Schedule
- Evaluation Criteria

1.2   Background

This section provides an overview of the literature related to VOC health effects, VOC contaminant removal by adsorption processes, and adsorption system design. These items will assist in recognizing VOC contaminants, identifying the ability to remove VOCs from water supplies using adsorption processes, and describing the mechanisms that will help in qualifying and quantifying the removal efficiency of the adsorption process tested. VOCs are the volatile subset of synthetic

organic compounds (SOCs). Their volatility is a significant attribute that impacts occurrence and sample handling.

1.2.1 VOC Health Effects and Regulations

Since the mid 1970s, the U. S. Environmental Protection Agency (EPA) has focused on VOCs and SOCs in drinking water. EPA surveys showed that low concentrations of a wide variety of organic contaminants occur in surface and ground waters. Although the VOC and SOC concentrations have been reduced in more recent years as a result of more stringent standards under the Clean Water Act, their detection indicates that few water sources are completely protected from contamination.

Within the past decade, over 1,000 different VOCs and SOCs have been detected, often in minute amounts, in various drinking water supplies in the United States and abroad. Although the role of specific compounds in the development of cancer is poorly understood, the EPA has been working to reduce the exposure levels to these compounds and minimize risks to human health. One obvious strategy is to limit the presence of these compounds to the lowest levels possible. However, this approach may result in regulations that are difficult to implement. VOC regulations developed in the mid 1980s were based on the following three criteria:

- The analytical ability to detect the compound
- The potential health risk
- The potential for occurrence in a drinking water source.

Six national surveys of drinking water contamination were conducted by the EPA Office of Drinking Water between 1975 and 1981. Based on these surveys a list of contaminants was developed. These contaminants were then classified based on the strength of evidence of carcinogenicity. Based on this analysis the EPA promulgated The VOC Rule – Phase I of the Safe Drinking Water Act (SDWA). The VOC regulation established Maximum Contaminant Level Goals (MCLGs) and Maximum Contaminant Levels (MCLs) for eight compounds. Some VOCs were regulated by the EPA as part of the Phase II and V Rules of the SDWA. These regulations included MCLs for VOCs as listed in Tables A-1, A-2, and A-3 of Appendix A. Regulatory requirements continue to evolve as more information is gained. Appendix B lists VOCs that are proposed for regulation.

1.2.2 Adsorption Process

Four steps have been identified that must occur for organic materials to be removed from solution via adsorption. *First*, the organic material must be transported from the bulk solution to the stationary boundary layer of water around the adsorbent particle. *Second*, the organic material must diffuse through the boundary layer to the pore opening. *Third*, the organic material must be transported through the pore to a suitable surface site. *Fourth*, a physical bond between the organic material and the pore surface must form. The rate limiting steps are often boundary layer diffusion and pore transport.

During operation of a contactor containing fresh adsorbent, the adsorbent near the influent removes most of the organic material and little adsorption occurs in the water as it passes the rest of the contactor. As the adsorbent near the influent becomes saturated, organic material that is further down in the column is removed by the adsorbent. This progression occurs until the adsorbent is saturated or effluent concentration limits are exceeded, and the adsorbent must be regenerated.

1.2.3 Mass Transfer Zone

The region in the contactor where adsorption occurs is called the mass transfer zone (MTZ), as shown in Figure 1. If the rate limiting steps for adsorption are much faster than the rate at which the adsorbate is introduced, then the length of the MTZ (L_{MTZ}) approaches zero. More typically, the L_{MTZ} is long enough that the adsorbent contactor must be carefully designed to contain the MTZ.

In most cases, more than one type of organic compound is present and competition for available sites occurs. Such competition makes predictions of adsorbent bed life difficult. A careful evaluation of organic materials present and process objectives should be performed

1.2.4 Empty Bed Contact Time

As a rule, contactor depth should exceed the L_{MTZ} by enough to obtain reasonable bed life. The bed depth needs to be determined for each application, but some guidance can be provided from previous work. To normalize bed depths for different loading rates, the concept of empty bed contact time (EBCT) is often used. EBCT is the volume of the adsorbent divided by the flow rate. Consistent units must be used to result in a measure of time. Equations for EBCT are as follows:

$$EBCT = V/Q = L_{Bed}/(Q/a) = L_{Bed}/\text{loading rate}$$

Where: EBCT = empty bed contact time;

V = volume of bed occupied by the adsorbent;

Q = flow rate;

L_{Bed} = length of adsorbent bed; and

a = area of bed.

The EBCT affects the cost and performance of a GAC system. Too small an EBCT will result in frequent adsorbent replacement/reactivation resulting in higher operation and maintenance costs. Too great an EBCT will result in unnecessary capital cost for the contactors. These relationships are shown in Figure 2. EBCT requirements will vary from one application to the next, but a typical range is 10 to 30 minutes. Loading rates typically range from 2 to 10 gpm/ft^2 (4.89 to 24.5 m/hr).

1.2.5 Breakthrough Curves

During the operation of an adsorbent contactor, the concentration of adsorbate in the influent and the effluent can be monitored and plotted as a function of volume of water treated. Using a parameter called bed volumes can normalize the volume of water treated. The number of bed volumes treated should equal the volume of water treated divided by the volume of the contactor that is occupied by the adsorbent in the contactor. Such a curve, shown in Figure 3, is called a
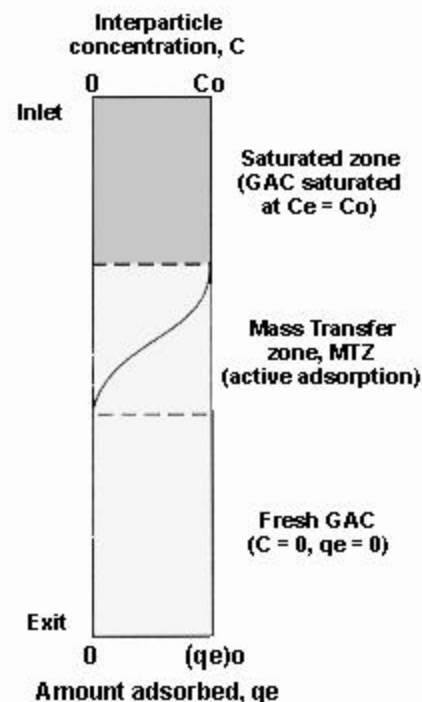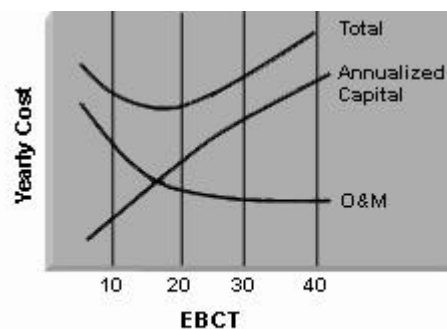

Figure 1
Mass Transfer Zone

Figure 2
Effect of EBCT on Cost

breakthrough curve. Breakthrough curves are often generated by pilot-scale contactors to develop design criteria for full-scale systems. Breakthrough occurs when the concentration of the target compound in the treated water reaches the treatment objective. Exhaustion occurs when the effluent concentration of the target compound is approximately the same as the influent concentration.

The breakthrough curve is often used to determine the adsorbent usage rate (AUR). The AUR is the mass of adsorbent required to treat a specific volume of water to a predetermined quality. High values of adsorbent usage result in increased operation and maintenance costs caused by more frequent adsorbent replacement. The AUR can be calculated as follows:
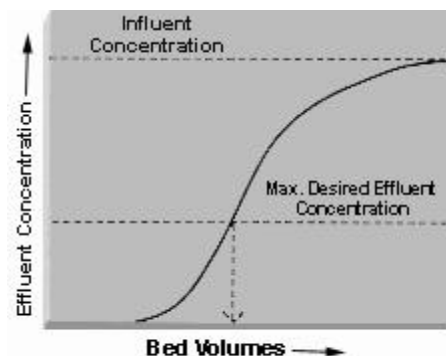
Figure 3
Typical Breakthrough Curve

AUR = mass of adsorbent/volume of water treated until breakthrough

The volume of water treated can be obtained from the breakthrough curve. First, an acceptable effluent concentration of adsorbate must be determined. Typically called the treatment objective or the breakthrough concentration, this concentration will determine the volume of water that can be treated by the mass of adsorbent used in the test. Usage rates are typically calculated from pilot-plant data to estimate the capital and operations costs for reactivating or replacing the adsorbent.

The capacity of the adsorbent for a specific compound (under the conditions of the column test) can be estimated from breakthrough curves by the following equation assuming all of the influent compound is adsorbed (as opposed to being removed by another mechanism such as biodegradation).

adsorbent capacity (mass compound/mass adsorbent) = influent concentration/AUR

Adsorbent capacity determined in pilot studies can be used to estimate AUR under various influent concentrations, provided that capacity does not change significantly with influent concentration.

1.2.6 Types of Adsorbents

Perhaps the most widely used adsorbent is granular activated carbon (GAC). GAC is typically made from wood, peat, lignite, subbituminous coal, or bituminous coal. The precursor material is first converted to a char and then carefully oxidized to develop internal pores. The high surface area associated with the pores in activated carbon is responsible for the removal of organic compounds. A handful of activated carbon may have a pore area equal to several football fields.

Synthetic resins have also been used as adsorbents. Many types are available based on the type of material used to make up the resin and resulting functional groups.

1.2.7 Reactivation

Once the concentration of the target compound in the effluent water form the contactor reaches the stated treatment objective, the adsorbent is taken off-line and regenerated or replaced with fresh adsorbent. Some adsorption systems, especially resins, are designed to provide regeneration in-place. Normally, in-place reactivation is produced by addition of a strong base solution or a solvent such as acetone or isopropanol to the adsorbent bed. The ability of the regeneration step to restore the resin's capacity is of primary importance and is included as part of the performance testing.

2.0   GENERAL APPROACH

Testing of equipment covered by this Verification Testing Plan shall be conducted by an NSF-qualified Field Testing Organization that is selected by the equipment Manufacturer. Water quality analytical work performed in conjunction with this Verification Testing Plan shall be contracted with a State-certified or third party or EPA-accredited laboratory.

The FTO shall provide full detail of the procedures to be followed for each task in the FOD. The FTO shall specify the operational conditions to be evaluated during the Equipment Verification Testing.

In general, the equipment verification testing approach consists of conducting an adsorption treatment pilot study of a water containing VOCs. The pilot plant shall be representative of the equipment Manufacturer's system. The minimum pilot testing period required by this Verification Testing Plan is intended to evaluate the system's mechanical and hydraulic integrity and operability under field conditions and to assess performance for the initial 2 months of operation. Ideally, pilot testing would allow determination of the breakthrough characteristics for target VOCs, but this may not occur within the 2-month test period. Consequently, a longer operation period or influent water spiking are offered as optional methods for achieving breakthrough. For adsorption systems incorporating in-place media regeneration, the effectiveness of regeneration should also be assessed.

A key decision point for the design and duration of the Equipment Verification Testing is establishing the overall goal of the test. Options include (a) demonstrating system integrity and initial performance by running the test for the minimum duration of 2 months, (b) evaluating adsorbent usage rate and adsorption capacity by testing until breakthrough of the critical VOC in the source water, or (c) evaluating adsorbent usage rate and adsorption capacity by spiking the influent water and testing until the amended VOC compound breaks through. The claims made by the manufacturer would be differing depending on which option was chosen. Examples of the claims that might be made for each of these options are as follows:

- Option a – "The structural and mechanical components of this system have been shown to pass up to "x" gpm of water with a turbidity of "t" and a total suspended solids (TSS) of "s" without sudden surges in flow, excessive headloss or leaks. The valves supplied with the unit worked well without leaking and with good reliability. The system as supplied provided the flexibility to operate under all the conditions envisioned including, parallel operation, lead-lag operation, and backwashing of one unit while the other unit was in service. The contactors had the necessary features to easily add and remove the adsorption media. The appurtenances were appropriate in size and function for the processing of the design flow. During the two months of operation all VOCs remained below detection in the treated water. The influent water contained the following VOCs: (list to follow).

- Option b – "The same statement from Option a plus "The media treated 500,000 gallons (10,000 bed volumes) of water when operated in a lead lag mode before media replacement or reactivation was needed. The VOC that first experienced breakthrough was 1,1-chicken wire, which was present in the influent at "y" mg/L. The water had a background dissolved organic carbon (DOC) of "z" mg/L and contained 12 other VOCs ranging in concentration from "a" to "z" ug/L. *State the performance of the in-situ regeneration system if one is provided.* The in-situ reactivation system restored the media to near-original condition during the three regeneration cycles tested."

- Option c – "The same statement from Option a plus "The media treated 500,000 gallons (10,000 bed volumes) of water that had been spiked with "y" mg/L of 1,1-chickenwire. The system was operated in a lead-lag arrangement. The water had a background DOC of "z" mg/L. The in-situ reactivation system restored the media to near-original condition during the three regeneration cycles tested."

The verification statement should include any significant side impacts caused by water quality changes in addition to changes in the VOC concentration. This would include impacts to the corrosivity of the water that may require corrective action before entering the distribution system.

3.0   OVERVIEW OF TASKS

This NSF Equipment Verification Testing Plan is divided into six tasks. A brief overview of the tasks to be included in the Verification Testing program is presented below:

3.1   Task 1: Feed Water Characterization

The objectives of this task are to characterize the feed water to be used in testing and measure the influent characteristics during equipment operation. The feed water shall be characterized for pertinent chemical parameters before beginning treatment system operation. Results of these analyses will be used to determine feed water pretreatment requirements, identify the individual VOC compounds requiring treatment (target VOCs) and the compounds most challenging to adsorption treatment (critical VOCs), and estimate run time and throughput until VOC breakthrough. In the case of Option c, where a VOC is spiked into the water, this task will serve to verify the spike concentration. The adsorption process influent characteristics shall be analyzed at selected intervals throughout the test run to allow assessment of system performance and adsorption capacity. The requirements for monitoring feedwater during the operation of the pilot are discussed later in the Operation section.

3.2   Task 2: System Design and Operation

The objectives of this task are to establish and document design and operating parameters for Verification Testing. These parameters will be used to guide operation of the adsorption equipment in treating the test feed water and collection of treatment operation and performance data.

3.3   Task 3: Treated Water Quality

The objectives of this task are to collect and analyze treated effluent water quality data. Effluent water quality shall be monitored at selected intervals during the testing run to evaluate treatment performance versus time of operation and throughput water volume.

3.4   Task 4: Adsorptive Media Regeneration

Some candidate treatment systems may use adsorptive resins that can be regenerated in-place, and incorporate regeneration capability as an integral part of the equipment. In such cases, the objective of this task is to evaluate regeneration effectiveness and characterize any residuals produced during regeneration.

3.5   Task 5: Data Management

The objective of this task is to establish an effective field protocol for data management at the field operations site and for transmission of data obtained during the Verification Testing between the FTO and NSF.

3.6   Task 6: Quality Assurance/Quality Control

An important aspect of Verification Testing is the protocols developed for quality assurance and quality control. The objective of this task is to assure accurate measurement of operational and water quality parameters during Verification Testing.

4.0   TESTING PERIOD

Guidelines for adsorptive media equipment Verification Testing duration are given below. The number and length of test runs conducted will depend, to some extent, on how rigorous a demonstration the equipment Manufacturer wishes to perform, and how strong a claim the Manufacturer would like to be able to make about equipment performance.

A test run shall consist of operating the treatment equipment for two months of actual run time, the minimum required testing duration to satisfy the requirements of this Equipment Verification Testing Plan. Although two months of pilot plant operation are adequate to verify system integrity (e.g., mechanical and hydraulic functioning, excessive headloss, channeling, etc.), it is likely that VOCs occurring in many natural source waters will not break through within two months of operation. It should be recognized by equipment Manufacturers that a claim that their adsorption system could treat a natural source water effectively for two months without exhibiting VOC breakthrough may not be overly impressive. For this reason, two options are provided for making the test more rigorous (and thereby strengthening the claim a Manufacturer could make): (a) operating the test equipment for a longer duration to achieve breakthrough of VOCs in the source water, or (b) spiking the influent water with a selected VOC compound to accelerate breakthrough.

For tests having the objective of operating until VOC breakthrough and determining breakthrough characteristics, the following "quit" criteria can be used to determine when to terminate operation (adopted from U.S. EPA 1996a). The pilot study can be concluded when the effluent concentration of the critical VOC is (a) ≥70% of the average influent concentration on two consecutive sampling dates at least 2 weeks apart, or (b) ≥50% of the average influent concentration and a plateau is reached in which the effluent concentration does not increase over 30 days by more than 10% of the average influent concentration.

For tests not running until breakthrough, it may be possible for the Manufacturer to provide an estimate of adsorbent usage rates and adsorption capacities from existing data for the VOC of interest and the type of adsorbent used.

5.0   DEFINITIONS OF OPERATIONAL PARAMETERS

The following definitions are used to describe operation and performance of an adsorptive media treatment system.

a – area

Adsorbent capacity or adsorption capacity – mass of solute adsorbed per unit mass of adsorbent, at breakthrough or at exhaustion.

Adsorbent Usage Rate (AUR) – the mass of adsorbent required to treat a specific volume of water to a predetermined quality.

Bed volume – a normalized unit of throughput, defined as run time divided by EBCT

Breakthrough – when the concentration of a target compound in the treated effluent reaches its treatment objective (e.g., MCL).

Breakthrough curve – A plot of concentration of an adsorbate of interest versus either run time or throughput (often in bed volumes) extending past the point where breakthrough occurs and usually to saturation. The resulting curve is characteristic of the adsorbent, adsorption system, and the influent water quality.

Ce – the concentration of the target compound after treatment by the adsorbent.

Co – the concentration of the target compound before treatment by the adsorbent.

Critical or controlling VOC – the one (or more) VOC compound in the influent water that breaks through first and, therefore, controls adsorbent replacement or regeneration.

Empty Bed Contact Time (EBCT) – the hydraulic retention time of an empty adsorber, defined as volume of the contactor occupied by the adsorbent divided by the flow rate.

Exhaustion or saturation – normally defined as when the effluent concentration of a target compound (e.g., VOC) is equal to its influent concentration, indicating that no adsorption is occurring. In practice, effluent concentrations may reach a plateau lower than the influent concentration because of other removal mechanisms, such as biodegradation.

gpm – gallons per minute

Loading rate – the velocity at which water is loaded to the contactor, typically in units of gpm/sf or m/min.

m – meters

min – minute

Q – flow rate

qe – the concentration of the target compound on the adsorbent in units of mass/mass.

Target VOCs – the VOC compounds present in the source water at concentrations greater than their treatment objectives and, therefore, requiring treatment.

V – volume

6.0   TASK 1: FEED WATER CHARACTERIZATION

6.1   Introduction

This task includes characterization of the feed water prior to testing and periodic analysis of the influent to the adsorption process throughout the test run. The feed water is the water fed to the treatment system in Equipment Verification Testing. The feed water and adsorption process influent may or may not be identical, depending on whether the treatment equipment incorporates pretreatment (such as filtration) into the packaged or modular system. It is assumed that the feed water will come from an actual water supply source. The FTO shall provide a description in the FOD of the feed water source, the feed water sampling point (if within an existing water treatment plant), and any pretreatment performed on the water prior to collection.

6.2   Objectives

The objectives of this task are to:

- Characterize the feed water before testing to provide information required to develop the test design

- Review historical data (where available) to assess seasonal variations and verify the representativeness of the feed water characterization results

- Assess pretreatment requirements, if any

- Identify target VOCs and critical VOCs

- Estimate the test run time and throughput volume to VOC breakthrough

- Analyze the adsorption process influent at selected intervals throughout the test run to determine influent characteristics and variability, and to obtain data needed to evaluate VOC removal and adsorption capacity (when used in conjunction with effluent data)

6.3   Work Plan

The work activities of this task are described below.

Pre-test feed water characterization. One or more grab samples of the feed water shall be collected and analyzed for the water quality characterization parameters in Table 1. The list of parameters shown in Table 1 should be considered minimum requirements for characterization, and Manufacturers intending to conduct equipment verification testing for applications other than VOC removal may wish to analyze the feed water for additional parameters. Analysis of synthetic organic chemicals (SOCs) is recommended if historical data are not available.

| | TABLE 1 | |
| | Feed Water/Influent Sampling and Analysis Plan | |

| | Required Minimum Number of Samples | |
Parameter	Pre-Test Feed Water Characterization	During-Test Influent Analysis
VOCs	1 or 2[a]	8[b]
TOC	1 or 2[a]	8[b]
UV254	1 or 2[a]	8[b]
Temperature	1 or 2[a]	8[b]
pH	1 or 2[a]	8[b]
Alkalinity	1 or 2[a]	3[c]
Total hardness	1 or 2[a]	3[c]
Calcium hardness	1 or 2[a]	3[c]
Turbidity	1 or 2[a]	3[c]
TSS	1 or 2[a]	3[c]
TDS or conductivity (optional)	1 or 2[a]	3[c]
Ammonia (optional)	1 or 2[a]	3[c]

[a] A minimum of 2 samples should be taken when historical data are not available.
[b] See Subsection 6.4. Collected at the same time as effluent samples.
[c] Collected at evenly spaced intervals throughout the test run.

Historical data review. Historical water quality data for the feed water shall be reviewed, where available, to evaluate trends in key parameters such as VOCs and total organic carbon (TOC), and to determine if the water quality measured by the grab samples is representative of the recent historical data.

Pretreatment requirements assessment. The need for pretreatment of the feed water prior to treatment in the adsorption equipment shall be assessed based on the characterization data. The need for pretreatment must be determined on a case-by-case basis because some packaged/modular adsorption systems may incorporate pretreatment and tolerances may differ among equipment. The most likely type of pretreatment is particle removal from turbid feed waters to avoid excessive fouling and reduce backwashing requirements. As a general rule, pretreatment for particle removal before adsorption should be considered if the feed water turbidity exceeds 5-10 ntu or if the feed water TSS exceeds 5 mg/L. The equipment Manufacturer may also provide pretreatment guidelines. Other possible characteristics that may require pretreatment to prevent scaling/fouling include elevated levels of hardness, iron, manganese, or readily-biodegradable organics in the feed water.

Target and critical VOC identification. Target VOCs are defined here as the VOC compounds whose influent concentrations exceed their treatment objectives, and therefore require treatment to produce finished water of acceptable quality. They are identified by comparing the concentrations of VOCs detected in feed water during characterization to their respective MCLs.

The critical or controlling VOC is defined here as the one or more individual compound that is expected to be most difficult to treat to the acceptable level via the adsorption process. Assessment of critical VOCs makes use of adsorption isotherm data, if available. The most commonly used isotherm model for liquid-phase adsorption is the Freundlich equation:

[1]
$$\frac{x}{m} = KC_e^{1/n}$$

> Where: x = mass of solute adsorbed;
>
> m = mass of adsorbent;
>
> C_e = equilibrium concentration of solute in liquid; and
>
> K and 1/n = empirical constants characteristic of the system.

Using Equation [1], the adsorbent loading (x/m) for an individual VOC can be estimated for a chosen C_e if the constants K and 1/n are known. A procedure for tentatively identifying the critical VOCs is outlined below.

1. Choosing C_e as the MCL, compute the estimated adsorbent loading at breakthrough as: $(x/m)_{bt} = K(MCL)^{1/n}$

2. Determine the amount of removal required to meet the MCL by subtracting the MCL concentration from the measured concentration in feed water: $\Delta C_{MCL} = C_o - MCL$

3. Calculate the volume of water treated at breakthrough per unit weight of adsorbent by dividing the carbon loading at breakthrough by the required removal: $(V/m)_{bt} = (x/m)_{bt}/\Delta C_{MCL}$

4. Identify the critical VOCs as the compounds with the lowest $(V/m)_{bt}$ values

A simple spreadsheet can be set up as shown in Table 2 to perform these computations for a number of compounds. Table 2 shows the source of input values and calculation formulas, as well as example calculations for two VOCs. In the example given, trichloroethylene (TCE) would be considered the more critical or controlling VOC at breakthrough because a lower volume of feed water could be treated per unit mass of adsorbent $[(V/m)_{bt}]$ at TCE breakthrough than at toluene breakthrough. A similar set of calculations can be performed for the 50% exhaustion condition instead of the breakthrough condition. It is interesting to note that for the example given the situation is reversed for 50% exhaustion: a higher volume of water could be treated at 50% TCE saturation than at 50% toluene saturation. These calculations should only be used as rough predictions because isotherm data are developed using specific adsorbent, single-solute solutions, solutions in distilled water devoid of extraneous TOC, and equilibrium conditions (whereas flow-through adsorbers are non-equilibrium systems). The critical VOC should be confirmed from empirical data during the pilot test.

For GAC, the isotherm constants K and 1/n have been determined for a large number of VOCs and can be found in the literature (e.g., U.S. EPA 1980; The Hazardous Waste Consultant 1986; Faust and Aly 1987; AWWA 1990; The Air Pollution Consultant 1992). Carbon vendors may also be sources for isotherm data. For adsorptive media other than GAC, adsorption isotherm data, or a relationship to GAC adsorptive properties, would have to be obtained from the media manufacturer.

			VOC Compound (Examples)	
TABLE 2 Calculations for Identifying Critical VOCs and Estimating Test Run Time				
Parameter	**Units**	**Formula or Source of Value**	**Chlordane**	**PCP[b]**
Parameter	Units	Value	Toluene	TCE
Feed water concentration, C_o	mg/L	Measured	5.0	0.5
Critical or required final concentration, $C_{f,MCL}$	mg/L	MCL	1.0	0.005
Final concentration for 50% reduction, $C_{f,50}$	mg/L	$0.5C_o$	2.5	0.25
Critical or required reduction, ΔC_{MCL}	mg/L	C_o-MCL	4.0	0.495
Reduction for 50% removal, ΔC_{50}	mg/L	$0.5C_o$	2.5	0.25
K (Freundlich isotherm constant)		Literature[a]	26.1	28.0
1/n (Freundlich isotherm constant)		Literature[a]	0.44	0.62
Adsorbent loading @ breakthrough, $(x/m)_{bt}$	mg/g	$(K)(C_{f,MCL})^{1/n}$	26.10	1.05
Adsorbent loading @ 50% exhaustion, $(x/m)_{50}$	mg/g	$(K)(C_{f,50})^{1/n}$	39.06	11.85
Volume treated per media wt. @ breakthrough, $(V/m)_{bt}$	L/g	$(x/m)_{bt}/\Delta C_{MCL}$	6.53	2.12
Volume treated per media wt. @ 50% exhaustion, $(V/m)_{50}$	L/g	$(x/m)_{50}/\Delta C_{50}$	15.62	47.42
Mass of media in adsorber, m	g	Design param.	4500	4500
Flow rate, Q	L/min	Design param.	0.67	0.67
Estimated volume treated @ breakthrough, V_{bt}	L	$[(V/m)_{bt}][m]$	29363	9531
Estimated volume treated @ 50% exhaustion, V_{50}	L	$[(V/m)_{50}][m]$	70308	213380
Estimated run time @ breakthrough, t_{bt}	hr	$V_{bt}/60Q$	730	237
Estimated run time @ 50% exhaustion, t_{50}	hr	$V_{50}/60Q$	1749	5308
[a] U.S. EPA 1980; adsorption isotherm constants developed using Calgon F300 GAC				
[b] PCP = pentachlorophenol, pH 7.0				

Breakthrough estimation. A method for estimating the test run time and throughput volume at breakthrough is shown in Table 2 and described below. This procedure is a continuation of the computational steps for identifying critical VOC described above.

1. Compute the estimated volume of feed water treated at breakthrough by multiplying the volume treated per weight of adsorbent by the weight of adsorptive media in the adsorber:

   $V_{bt} = (V/m)_{bt}(m)$

2. Compute the estimated run time at breakthrough by dividing the volume treated at breakthrough by the influent flow rate and converting units from minutes to hours: $t_{bt} = V_{bt}/60Q$

3. Repeat steps 1 and 2 for the 50% exhaustion condition, defined as $C_f = 0.5C_o$

The information generated by these calculations can be used to assess whether VOC breakthrough is expected to occur within the minimum pilot test duration of 2 months and, if not, roughly how long a run time would be required to achieve breakthrough. Depending on the overall test goal (see Section 2.0), these predictions can be used to estimate test duration, evaluate potential spiking results, and develop the sampling schedule (Subsections 6.4 and 8.4).

During-test influent analysis. Influent samples to the treatment process shall be collected during the test run and analyzed for the parameters shown in Table 1. This list of parameters should be considered minimum requirements for influent analysis, and Manufacturers intending to conduct equipment verification testing for applications other than VOC removal may wish to analyze the influent water for additional parameters. Influent samples shall be collected from the influent line to the adsorption treatment process (see sampling point 2 in Figure 4), subsequent to any pretreatment processes or VOC spiking.

FIGURE 4
EXAMPLE ADSORPTION TREATMENT SYSTEM SCHEMATIC
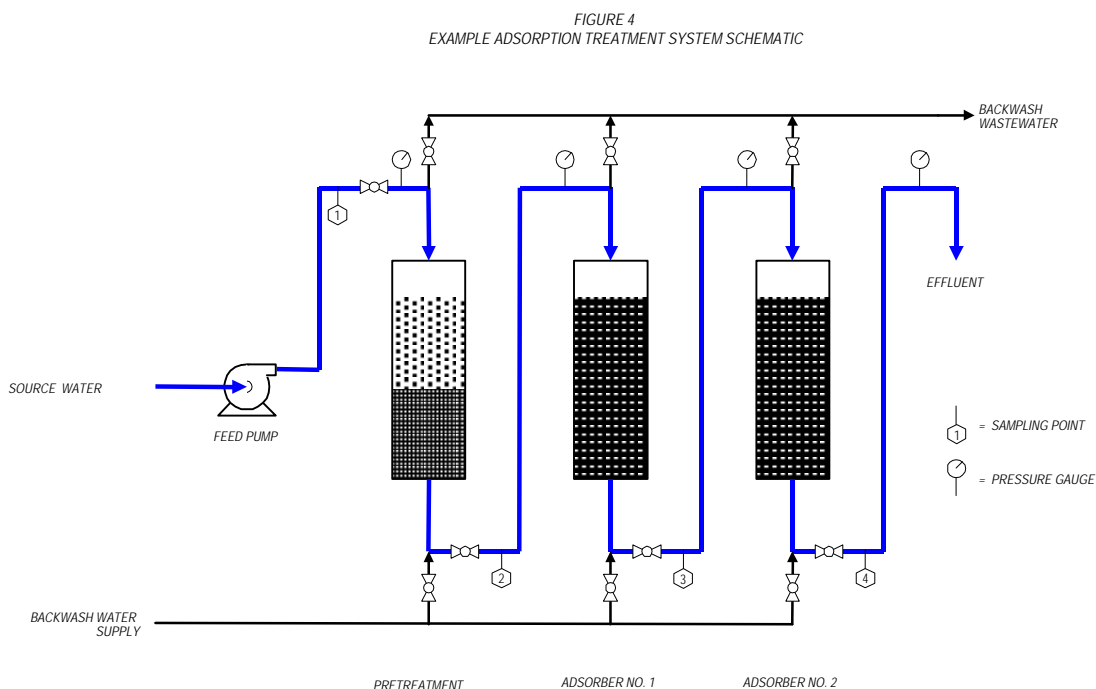
6.4   Analytical Schedule

Table 1 shows the sampling requirements for pre-test feed water characterization. For parameters where no historical data are available for comparison, at least two characterization samples collected at least 10 days apart are recommended to check sample representativeness.

Table 1 also shows the sampling requirements for during-test influent analysis. A minimum of 8 treatment system influent samples shall be collected and analyzed for VOCs, TOC, UV254, pH, and temperature during the equipment verification test run. Influent and effluent samples should be collected at the same time. For tests using the minimum required duration of 2 months, sampling and analysis for these parameters should be conducted at least once per week. For longer test durations, the estimated run time to VOC breakthrough should be used as a guide in developing the influent/effluent sampling schedule. As the test results approach breakthrough and the quit criteria (Section 4.0), it may be desirable to collect samples more frequently than earlier in the testing period.

A minimum of 3 treatment system influent samples shall be collected and analyzed for alkalinity, total and calcium hardness, turbidity, TSS, total dissolved solids (TDS) or conductivity (optional), and ammonia (optional) during the test run. The sampling times for these parameters should be distributed evenly over the testing period. Some treatment equipment may incorporate continuous or automated monitoring of temperature, pH, conductivity, turbidity, or other parameters, which would allow more frequent data collection than that specified above.

6.5   Evaluation Criteria

Feed water quality will be evaluated within the context of the Manufacturer's statement of performance capabilities. The feed water should challenge the capabilities of the treatment equipment with respect to VOC and TOC concentrations but should not be beyond the ranges suitable for treatment by the equipment in question. Other evaluation criteria are given below.

- Pretreatment for particle removal may be indicated if the feed water turbidity is greater than 5-10 ntu or TSS exceeds 5 mg/L. However, Manufacturer specifications regarding pretreatment for particulates or other constituents should be followed in any case.

- Pretreatment for hardness may be indicated if the feed water hardness is greater than manufacturers recommendations or the pH, alkalinity and hardness measurements indicate that the water is not stable.

- pH adjustment may be indicated if the pH is outside manufacturers recommendations. Water pH can impact adsorption efficiency and, at extremes, may pose a corrosion hazard to equipment. The manufacturer may wish to adjust the pH.

- Target VOCs are identified as VOC compounds with measured concentrations in feed water that exceed their respective MCLs. MCLs for VOCs are tabulated in Appendix A.

- Critical or controlling VOCs in feed water are identified as the compounds with the lowest predicted values of the parameter $(V/m)_{bt}$ or V_{bt}.

- Estimated test run times until breakthrough and 50% exhaustion can be used to establish the test run time and sampling plan for test durations longer than two months. This information can also be used to assess the desirability of spiking and the appropriateness of treating the feed water by the adsorption process (if, for instance, rapid breakthrough is predicted).

7.0   TASK 2: SYSTEM DESIGN AND OPERATION

7.1   Introduction

The design and operating parameters of the adsorptive media treatment system being verified will be delineated under this task.

7.2   Objectives

The objectives of this task are to:

- Document treatment system design parameters.
- Describe system start-up and operations and maintenance (O&M) procedures
- Develop an operations monitoring plan

7.3 Work Plan

The FOD shall specify information concerning design and operation of the adsorption system being evaluated. The work activities of this task are described below.

System design parameters. The FTO shall document the equipment verification study design data shown in Table 3. Figure 4 is an example schematic of a typical adsorption treatment system showing sampling points. The FTO should provide a similar schematic depicting the actual adsorptive media treatment system to be tested, including any pretreatment processes and VOC spiking used, in the FOD.

Parameter	Units	Value or Description
TABLE 3 Test System Design Data		
General		
Test location	--	
Utility name	--	
Water source	--	
Feed mode (semi-batch or continuous)	--	describe
Spiked VOC compound, if any	--	
Spike target concentration	μg/L	
Spiking method	--	describe
Pretreatment processes	--	describe, if any
Adsorptive Media		
Media manufacturer	--	
Media type and trade name	--	
Mesh size	US std mesh sizes	upper x lower
Particle diameter	mm	
Apparent density	g/mL	
Adsorption System		
Number of adsorbers in series	--	
Adsorber dimensions	m	e.g., diameter and depth
Bed volume per adsorber (V_b)	L	
Volumetric flow rate (Q)	mL/min	
Empty bed contact time (EBCT)	min	$EBCT = V_b/Q$
Superficial velocity (v), also referred to as hydraulic loading rate	m/hr	$v = Q/A$, where A = bed cross sectional area
Mass of media (dry) per adsorber	g	
Regeneration system, regenerant fluid, and regeneration procedure	--	describe, if system has in-place regeneration capability

Start-up and O&M procedures. System start-up and O&M procedures based on Manufacturer specifications shall be described by the FTO in the FOD. Specific procedures for backwashing and regeneration shall be included. Start-up procedures may include bed preparation such as pre-wetting, degassing, and fines removal. Start-up itself will involve setting valves to the correct run status, starting the feed pump to deliver test water to the system, and adjusting the flow rate to the target value.

Operation with a continuous flow of test water from the source is preferable, but feeding from a batch-filled feed tank is acceptable. If a batch feed tank is used the residence time in the feed tank should be minimized to avoid volatilization losses of VOCs. The system flow rate should be adjusted as necessary during operation to maintain the target flow. The system should be operated continuously to the extent possible, and only shut down for backwashing, necessary maintenance, or regeneration (for in-place regenerable media). Any down time shall be recorded and not included in the cumulative run time or throughput volume calculations. The reason for each shutdown shall be documented. The adsorbers should be backwashed at least once during the testing period.

Operations monitoring plan. The FTO shall provide an operations monitoring plan in the FOD, including operational parameters to be monitored, monitoring points, and monitoring frequencies. At a minimum, flow rate, pressure before and after each adsorption or filtration bed and head loss (differential pressure) across each bed, influent temperature, and influent pH should be monitored routinely. Other parameters recommended by the Manufacturer should also be included. Influent/effluent sampling times should also be specified in the monitoring plan.

7.4 Analytical Schedule

System flow rate, pressures and head loss across each bed, temperature, and pH should be measured either continuously or at least daily. Whenever a bed is backwashed, the head loss before and after backwashing should be recorded to evaluate its effectiveness. A record of the backwashing frequency and backwash water volume produced should also be maintained.

7.5 Evaluation Criteria

The system flow rate should be maintained within a range of ±5% of the target value. Criteria for backwashing are usually based on a head loss threshold and should be provided by the equipment Manufacturer. Quit criteria for determining when it is appropriate to terminate a test run intended to run until VOC breakthrough are given in Section 4.0. For systems with in-place regenerable media, regeneration criteria should also be provided by the Manufacturer, and should be based on VOC breakthrough.

8.0 TASK 3: TREATED WATER QUALITY

8.1 Introduction

This task involves sampling and analysis of treated effluent at selected intervals during system operation. The effluent water samples shall be analyzed for VOCs and other selected water quality parameters. The analytical results shall be used to evaluate system performance in terms of VOC removal, and, for tests running until breakthrough, the adsorbent usage rate and adsorption

capacity. For this type of test, the effluent results also shall be used to determine when it is appropriate to terminate the test run.

8.2   Objectives

The objectives of this task are:

- Collect effluent VOC data to evaluate treated water quality, removal across the system, and whether breakthrough occurs. For tests running to breakthrough, collect sufficient effluent data to accurately determine breakthrough characteristics for the critical VOC(s).

- Analyze the data to evaluate treatment system performance, adsorptive media service life until breakthrough, adsorbent usage rate, and adsorption capacity of the media.

8.3   Work Plan

The work activities of this task are described below.

Effluent analysis. Adsorption process effluent samples shall be collected during the test run and analyzed for the parameters shown in Table 4. This list of parameters should be considered minimum requirements for effluent analysis, and Manufacturers intending to conduct equipment verification testing for applications other than VOC removal may wish to analyze effluent samples for additional parameters. Effluent samples shall be collected from sampling points downstream from each adsorber in the system (e.g., sampling points 3 and 4 in Figure 4).

	Required Minimum Number of Samples		
Parameter	**Adsorber 1 Effluent**	**Adsorber 2 Effluent**	**Adsorber n Effluent[a]**
VOCs	8[b]	8[b]	8[b]
TOC	8[b]	8[b]	8[b]
UV254	8[b]	8[b]	8[b]

TABLE 4
Effluent Sampling and Analysis Plan

[a] Effluent from each adsorber in the system should be analyzed.
[b] See Subsection 8.4. Collected at the same time as influent samples.

8.4   Analytical Schedule

Table 4 shows the minimum effluent sampling requirements for treated water quality analysis. A minimum of 8 treatment system effluent samples shall be collected downstream from each adsorber and analyzed for VOCs, TOC, and UV254 during the equipment verification test run. Influent and effluent samples should be collected at the same time. For tests using the minimum required duration of two months, sampling and analysis for these parameters should be conducted at least once per week. For longer test durations, the estimated run time to VOC breakthrough should be used as a guide in developing the influent/effluent sampling schedule. As the test results approach breakthrough and the quit criteria (Section 4.0), it may be desirable to collect samples more frequently than earlier in the testing period.

8.5   Evaluation Criteria

Data analysis and interpretation for this task includes:

- Effluent VOC data shall be evaluated on a continuous basis to determine the critical or controlling VOC(s). The critical VOCs are those that breakthrough first – that is, appear in the effluent at concentrations exceeding their respective MCLs.

- For test runs operating for the minimum duration of two months and not reaching VOC breakthrough, the effluent data shall be evaluated in conjunction with the influent data to evaluate treatment performance (e.g., removal efficiency and treated water quality achieved).

- The effluent VOC data shall be used in conjunction with the quit criteria described in Section 4.0 to determine when to terminate the test run (for tests intended to run to breakthrough).

- Breakthrough curves - plots of effluent concentration versus operating time and versus throughput - shall be prepared for the critical VOCs. It is customary to express throughput as the number of bed volumes of water treated. Measured influent concentrations should also be shown on these plots for reference. Figure 5 shows an example breakthrough curve plot.

Figure 5
Example Breakthrough Curve

Adsorption capacity is calculated as the area between these two curves
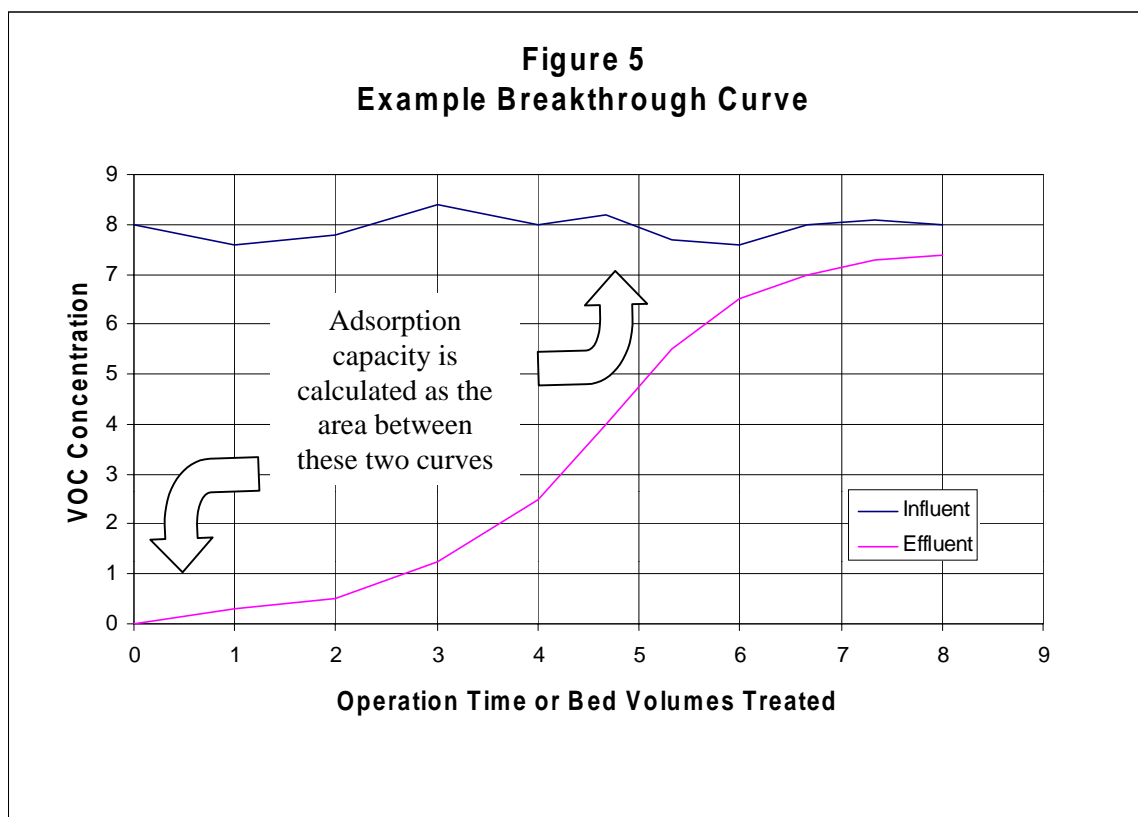
- If the manufacturer wishes only to make the claim that their equipment is hydraulically suited to treat the water, or is prepared to cite peer-reviewed (independent review by expert in field) support of carbon life, the test can be stopped in two months even if breakthrough has not occurred. If the manufacturer wishes to continue testing to make a stronger claim, they can use the criteria listed in Section 4 to determine when to stop testing. In this latter case, the adsorptive media service life until breakthrough shall be determined (from the breakthrough curves) in terms of operating time and throughput bed volumes. In addition to the breakthrough criteria, operating time and bed volumes treated until exhaustion should be estimated as when effluent concentrations reach a plateau where they are approximately

constant. This plateau effluent concentration for a given compound may be roughly equal to the influent concentration or somewhat less than that if biodegradation is occurring in the bed.

- The adsorbent usage rate (AUR) shall be calculated from the breakthrough data as:

[2]
$$\text{AUR [lbs/MG]} = \frac{(\text{media density [lbs/ft}^3\text{]})(133{,}670 \text{ ft}^3/\text{MG})}{(\text{bed volumes to breakthrough})}$$

- Adsorption capacity at breakthrough [$(x/m)_{bt}$] shall be calculated for the critical VOCs as:

[3]
$$(x/m)_{bt} = \left[\int_{t=0}^{t=t_{bt}} (C_o - C_e)\,dt \right]\left[\frac{Q}{m} \right]$$

Where: $(x/m)_{bt}$ = the mass of adsorbate adsorbed per mass of adsorbent at breakthrough;

C_o = influent concentration of VOC of given VOC;

C_e = effluent concentration of VOC of given VOC;

Q = nominal flow rate (assumed to be approximately constant); and

m = mass of adsorptive media in adsorber.

The integral quantity in equation [3] can be estimated from a breakthrough curve plot as the area between the C_o and C_e traces and bounded on the right by a vertical line drawn to intersect the point where C_e equals the breakthrough concentration. This same procedure can be used to estimate the adsorption capacity at exhaustion (saturation) and the total system adsorption capacity (i.e., mass of VOC adsorbed in all adsorbers when the final adsorber reaches breakthrough).

9.0   TASK 4: ADSORPTIVE MEDIA REGENERATION

9.1   Introduction

This task is applicable only to adsorption treatment systems that use adsorptive media that can be regenerated in-place and that incorporate regeneration capability as an integral part of the equipment being tested. Manufacturers of this type of equipment have a choice of how to conduct verification testing. Testing can be conducted according to the guidelines given in Section 4.0, but these guidelines specify only one loading period and do not include evaluation of in-place regeneration of the adsorptive media. Alternately, if the Manufacturer wishes to make a claim about the in-place regeneration capability of the equipment, verification testing must include, as a minimum, an initial loading cycle, followed by a regeneration cycle, and a second loading cycle. The purpose of this additional requirement is to allow comparison of adsorptive media performance before and after regeneration. Special guidelines for testing this latter type of testing sequence are described under this task.

The regeneration system, regenerant fluids used, and regeneration procedure shall be documented as part of the **System Design and Operation** task (Section 7.0)

9.2   Objectives

The objectives of this task are to:

- Develop plans for the testing period and the sampling & analysis program (revised from guidelines presented earlier in this document to allow for in-place regeneration).

- Evaluate regeneration effectiveness with respect to adsorptive media performance before and after in-place regeneration.

- Characterize any residuals produced during regeneration.

9.3   Work Plan

The work activities for this task are described below.

Revised testing period. In order to evaluate and make a Manufacturer's claim regarding the in-place regeneration capability of adsorption equipment, testing must span, at a minimum, one sequence of loading/regeneration/loading of the adsorptive media. Each loading period shall run at least long enough to reach breakthrough of critical VOCs so that breakthrough characteristics can be determined. The loading period duration should be determined from regeneration criteria specified by the equipment Manufacturer or according to the quit criteria specified under Section 4.0. In either case, the entire test run duration shall be at least two months to meet the Verification Testing requirements. If the three-step procedure described above is completed in less than two months, the test should be extended to provide more regeneration/loading cycles. Incorporation of additional cycles into the testing program is desirable in that, if supported by the data, it would add more credence to a Manufacturer's claim of regeneration effectiveness and retention of adsorption capacity over time. Whether or not additional cycles are completed, the FTO must make a statement about the efficiency of regeneration. If the efficiency of regeneration is not studied as part of this test effort, or available from other studies, the FTO would have to say that regeneration efficiency is not known. For media that is well known, the statement can be based on the results of previous tests that have been peer reviewed. In this context, peer reviewed refers to results published in Journals that employ a review step by recognized experts before publishing submitted articles.

Revised sampling & analysis plan. The influent/effluent sampling & analysis guidelines described in Sections 6.0 and 8.0 shall be followed during the first loading period. If desired, to reduce cost, the number of required influent/effluent samples in subsequent loading periods can be reduced to a minimum of 5 samples per period provided the breakthrough characteristics are adequately measured. This reduction may be possible if the data from the first loading period allow a fewer number of samples to be strategically scheduled to define the shape of the breakthrough curve. The FTO is cautioned, however, that collecting fewer samples carries with it the risk of missing breakthrough.

Residuals characterization. Any residuals produced during in-place regeneration of the adsorptive media shall be fully characterized and documented with respect to quantity and VOC composition. For example, if an off-gas stream is produced by a high temperature gas purge of the media, the off-gas flow rate, duration, and total off-gas volume emitted should be measured, and sampling and analysis should be conducted to determine VOC concentrations and total VOC mass emissions. Likewise, if a solvent solution is used for regeneration, the quantity and characteristics of the regenerant before and after (including VOC concentrations) use should be measured and reported. The information from this residuals characterization task shall be used to determine the efficiency of regeneration. A mass balance approach shall be used to determine whether all the VOCs were removed during the regeneration process. If the mass of VOCs recovered in the regeneration stream is similar to the mass adsorbed, then the regeneration process was successful. If the mass of

VOCs in the regeneration stream is half of that adsorbed, then the regeneration process was probably not successful.

9.4   Analytical Schedule

The analytical schedule for influent/effluent samples during the first loading period shall be the same as described in Subsections 6.4 and 8.4. For subsequent loading periods, the required number of influent and effluent samples can be reduced to a minimum of five per loading period, and the sampling schedule should be based on the results of the first loading period in order to define the breakthrough curve of critical VOCs. The analytical parameters for influent and effluent samples shall be the same as described in Sections 6.0 and 8.0.

For characterization of regeneration residuals, a sampling and analytical plan shall be developed by the FTO in the FOD to thoroughly characterize the VOC content of the residual stream.

9.5   Evaluation Criteria

Verification testing evaluation of adsorption treatment systems with in-place regeneration includes the same types of data analysis and interpretation as described previously for standard (nonregenerable) adsorption systems, plus a comparative analysis of adsorption characteristics before and after media regeneration. The purpose of the comparative analysis is to assess/quantify whether any reduction of adsorptive media service life or adsorption capacity occurs as a result of in-place regeneration. This shall be evaluated by determining the media service life, in terms of operating time and bed volumes of water treated until breakthrough (and until exhaustion, if the data allow), for the initial and subsequent loading periods and quantitatively comparing the results. Similarly, the adsorption capacity before and after regeneration can be determined and compared. Procedures for determining media service life and adsorption capacity are described in Subsection 8.5. In addition, a mass balance should be developed for critical VOCs to evaluate the completeness of regeneration. Equation 4 describes the mass balance in quantitative terms:

[4] $E_{regen} = [(\text{mass adsorbed} - \text{mass removed})/\text{mass adsorbed}](100\%)$

Where: E_{regen} = the regeneration efficiency;

mass adsorbed = the mass of VOC adsorbed to the carbon as calculated from equation 3;

mass removed = the mass of VOC recovered in the regeneration stream.

10.0   TASK 5: DATA MANAGEMENT

10.1   Introduction

The data management system used in the verification testing program shall involve the use of computer spreadsheets, manual recording methods, or both, for recording operational parameters for the adsorptive media treatment equipment on a daily basis.

10.2   Objectives

The objective of this task is to establish a viable structure for the recording and transmission of field testing data such that the FTO provides sufficient and reliable operational data to the NSF for verification purposes.

10.3   Work Plan

The following protocol has been developed for data handling and data verification by the FTO. Where possible, a Supervisory Control and Data Acquisition (SCADA) system should be used for automatic entry of testing data into computer databases. Specific parcels of the computer databases for operational and water quality parameters should then be downloaded by manual importation into Microsoft Excel or similar spreadsheet software. These specific database parcels shall be identified based upon discrete time spans and monitoring parameters. In spreadsheet form, the data shall be manipulated into a convenient framework to allow analysis of equipment operation. Backup of the computer databases to diskette should be performed on a weekly basis, at a minimum.

In the case when a SCADA system is not available, field testing operators shall record data and calculations by hand in laboratory notebooks (daily measurements shall be recorded on specially prepared data log sheets as appropriate). The laboratory notebook will provide carbon copies of each page. The original notebooks shall be stored on-site; the carbon copy sheets shall be forwarded to the project engineer of the FTO at least once per week. This protocol will not only ease referencing the original data, but offer protection of the original record of results. Pilot operating logs shall include a description of the adsorptive media treatment equipment (description of test runs, names of visitors, description of any problems or issues, etc.); such descriptions shall be provided in addition to experimental calculations and other items.

The database for the project shall be set up in the form of custom-designed spreadsheets. The spreadsheets shall be capable of storing and manipulating each monitored water quality and operational parameter from each task, each sampling location, and each sampling time. All data from the laboratory notebooks and data log sheets shall be entered into the appropriate spreadsheet. Data entry shall be conducted on-site by the designated field testing operators. All recorded calculations shall also be checked at this time. Following data entry, the spreadsheet shall be printed out and the printout shall be checked against the handwritten data sheet. Any corrections shall be noted on the hard copies and corrected on the screen, and then a corrected version of the spreadsheet shall be printed out. Each step of the verification process shall be initialed by the field testing operator or engineer performing the entry or verification step.

Each sample shall be assigned a unique identification (ID) number that shall then be tied to the data from that experiment through each step of data entry and analysis. As samples are collected and sent to a State-certified or third party- or EPA- accredited laboratory, the data shall be tracked by use of the same system ID numbers. Data from the outside laboratories shall be received and reviewed by the field testing operator. These data shall be entered into the data spreadsheets, corrected, and verified in the same manner as the field data.

11.0   TASK 6: QUALITY ASSURANCE/QUALITY CONTROL

11.1   Introduction

Quality assurance and quality control (QA/QC) of the operation of the adsorptive media treatment equipment and the measured water quality parameters shall be maintained during the verification testing program.

11.2   Objectives

The objective of this task is to maintain strict QA/QC methods and procedures during the Equipment Verification Testing Program. Maintenance of strict QA/QC procedures is important, in that if a question arises when analyzing or interpreting data collected for a given experiment, it will be possible to verify exact conditions at the time of testing.

11.3   Work Plan

Equipment flow rates and associated signals should be verified and verification recorded on a routine basis. A routine daily visual check during testing shall be established to verify that each piece of equipment or instrumentation is operating properly. Particular care shall be taken to verify that any chemicals are being fed at the defined flow rate into a flow stream that is operating at the expected flow rate, such that the chemical concentrations are correct. In-line monitoring equipment such as flow meters, etc., shall be checked to verify that the readout matches with the actual measurement (i.e. flow rate) and that the signal being recorded is correct. The items listed are in addition to any specified checks outlined in the analytical methods.

Daily QA/QC Verifications.

- Feed pump flow rate - verified volumetrically over a specific time period
- On-line turbidimeter flow rates (if used) - verified volumetrically.

Weekly QA/QC Verifications.

- In-line flow meters/rotameters - clean equipment to remove any debris or biological buildup and verify flow volumetrically to avoid erroneous readings.

- Recalibration of on-line pH meters, conductivity meters, and/or turbidimeters (if used).

- Tubing - verify good condition of all tubing and connections, replace if necessary

Quarterly QA/QC Verifications.

- On-line turbidimeter (if used) - clean out reservoirs and recalibrate.

- Differential pressure transmitters (if used) - verify gauge readings and electrical signal using a pressure meter.

On-Site Analyses. The analytical methods utilized in this study for on-site monitoring of influent and effluent water quality are described below. Use of either bench-top or on-line field analytical equipment will be acceptable for the verification testing; however, on-line equipment is recommended for ease of operation. Use of on-line equipment is also preferable because it reduces the introduction of error and the variability of analytical results generated by inconsistent sampling techniques.

> **pH.** Analyses for pH shall be performed according to Standard Method 4500-H$^+$ (APHA et al., 1998). A 2-point calibration of the pH meter used in this study shall be performed once per day when the instrument is in use. Certified pH buffers in the expected range shall be used. The pH probe shall be stored in the appropriate solution defined in the instrument manual.

> **Temperature**. Temperature measurements shall be made in accordance with Standard Method 2550. The thermometer used should be a high-quality, mercury-

filled, Celsius thermometer with a scale marked for every 0.1°C and covering the range of expected temperatures, with markings etched in the glass. The thermometer should be checked periodically against a precision thermometer certified by the National Institute of Standards and Technology (NIST). An on-line thermometer is acceptable for this work.

Turbidity. Turbidity analyses shall be performed according to Standard Method 2130 with either an on-line or bench-top turbidimeter. The turbidimeter shall be calibrated over the expected range of sample measurements at the beginning of testing and at least weekly thereafter. The turbidimeter shall be re-calibrated whenever it is turned off and re-started. An on-line turbidity meter is acceptable for this work.

Off-Site Analyses. All off-site analytical work associated with equipment verification testing shall be performed by a State-certified or third party- or EPA- accredited laboratory. Sampling for off-site analysis shall be conducted using proper sampling techniques and samples shall be collected in appropriate volumes and containers provided by the laboratory. These samples shall be preserved, stored, shipped, and analyzed in accordance with appropriate procedures and holding times, as specified by the analytical lab. Table 5 presents a summary of sample containers/volumes, preservation methods, holding times, and analytical methods for the analytes required for this verification testing work.

				Analytical Methods	
Parameter	**Sample Size, Container**	**Preservation**	**Holding Time**	**Standard Methods**[a]	**EPA Method**[b,c,d]
VOCs	3-40 mL, G-TLC	HCl to pH<2, Cool to 4°C	14 d		8260B, 624
TOC	250 mL. P/G	H_2SO_4 to pH<2, Cool to 4°C	28 d	5310 C or D	415.1, 415.2
UV254	100 mL, G	None	48 h	5910 B	
Alkalinity	250 mL. P/G	Cool to 4°C	14 d	2320 B	310.1
Total hardness	100 mL, P/G	H_2SO_4 to pH<2	180 d	2340 C	130
Calcium hardness	500 mL. P/G	HNO_3 to pH<2	6 mo	3500-Ca	200.7
Turbidity	100 mL, P/G	Cool to 4°C	48 h	2130 B	180.1
TSS	250 mL. P/G	Cool to 4°C	7 d	2540 D	160.1
TDS	250 mL. P/G	Cool to 4°C	7 d	2540 C	160.2
Conductivity	250 mL. P/G	Cool to 4°C	28 d	2510 B	120.1
Ammonia	250 mL. P/G	H_2SO_4 to pH<2, Cool to 4°C	28 d	$4500-NH_3$	350.2, 350.3

TABLE 5
Analytical Methods and Sample Requirements

[a] APHA et al., 1998; [b] U.S. EPA, 1986b; [c] EPA, 1982; [d] EPA, 1983.
G-TLC = glass with Teflon-lined cap, P/G = polyethylene or glass.

Samples for VOCs analysis shall be collected so that turbulence is minimized and with zero headspace in 40-mL glass VOA vials with Teflon-lined silicone septum screw caps. A comprehensive Gas Chromatography/Mass Spectroscopy (GC/MS) method, such as EPA 8260B, should be used for VOCs analysis during initial characterization of feed water to capture the full range of potential VOC constituents. After characterization, it may be possible to employ a less-costly analytical method, such as EPA 601/602 or EPA 8010/8020, that will detect the VOCs actually present in the feed water.

12.0   OPERATION AND MAINTENANCE

The Field Testing Organization shall obtain the Manufacturer-supplied O&M manuals to evaluate the instructions and procedures for their applicability during the verification testing period. The following are recommendations for criteria for the evaluation of O&M manuals for package plants employing adsorptive media for VOC removal. The feedwater should be characterized before operation. The feedwater characterization requirements are discussed in Section 3.1.

12.1 Operation

The manufacturer shall provide readily understood information on the required or recommended procedures related to the proper operation of the package plant equipment, including, but not limited to, the following:

Monitoring of Preconditioning of Adsorptive Media:

- Utilize Manufacturer's Procedure which may vary depending upon adsorptive media selected

- Backwash Parameters (flow rate, time, backwash water turbidity, etc.)

- Pretreatment chemical application (chemical concentration, time, and flow rate)

- Volume of wastewater

- Wastewater disposal requirements (see Regeneration Wastewater Disposal below)

Monitoring Operation:

- Feed water VOC concentration

- Feed water pH

- Feed water adjusted pH

- Feed water flow rate

- Feed water pressure

- Treated water VOC concentration

- Treated water pH

- Treated water adjusted pH

- Treated water pressure

- Chemical feed rates

- Chemical consumption

- Electrical energy consumption

- Maintenance and operator labor requirements

- Spare parts requirements

Monitoring Regeneration of Adsorptive Media:

- Utilize manufacturer's procedure for regeneration which shall vary depending upon selected adsorptive media, equipment, and process variables

- Backwash parameters (flow rate, time, backwash water turbidity, etc.)

- Regeneration parameters (flow rate, time, regeneration chemical concentration and flow rate, effluent concentration, effluent pH, etc.)

- Neutralization Parameters (flow rate, time, neutralization chemical concentration and flow rate, (effluent concentration, effluent pH, adsorptive media depletion, etc.)

- Adsorptive media makeup requirement

Monitoring Regeneration Wastewater Disposal:

- Utilize manufacturer's procedure for processing, reclaiming, and/or disposing of regeneration wastewater, adsorptive media preconditioning wastewater, and waste solids, which shall vary depending upon selected adsorptive media, equipment, treatment chemicals and process variables

- pH adjustment parameters (flow rate, pH, time, pH adjustment chemical consumption, etc.)

- Flocculation/coagulation parameters (flow rate, time, flocculation/coagulation chemical consumption, etc.)

- Liquid/solid separation parameters (flow rate, time, etc.)

- Solids dewatering parameters (flow rate, time, sludge conditioning chemical consumption, dewatered sludge solids, content, toxicity of dewatered solids, etc.)

- Solids disposal parameters (volume, toxicity, permits, transportation of solids to disposal site, costs of transportation and disposal, etc.)

- Liquid disposal parameters (volume, toxicity, pH, permits, adjustment requirements, costs of disposal, etc.)

12.2   Maintenance

The manufacturer shall provide readily understood information on the required or recommended maintenance schedule for each piece of operating equipment including, but not limited to:

- pumps
- valves
- all chemical feed and storage equipment

- all instruments

The manufacturer shall provide readily understood information on the required or recommended maintenance schedule for non-mechanical or non-electrical equipment including, but not limited to:

- adsorptive media vessels
- feed lines
- manual valves

13.0 REFERENCES

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APPENDIX A - REGULATED VOCS

TABLE A-1 Summary of Compounds Regulated by VOC Rule			
VOC	**MCLG (mg/L)**	**MCL (mg/L)**	**Potential Health Effects**
Benzene	zero	0.005	Anemia; decrease in blood platelets; increased risk of cancer
carbon tetrachloride	zero	0.005	Liver problems; increased risk of cancer
p-dichlorobenzene	0.075	0.075	Anemia; liver, kidney or spleen damage; changes in the blood
1,2-dichloroethane	zero	0.005	Increased risk of cancer
1,1-dichloroethylene	0.007	0.007	Liver problems
1,1,1-trichloroethane	0.20	0.2	Liver, nervous systems or circulatory problems
trichloroethylene	zero	0.005	Liver problems, increased risk of cancer
Vinyl chloride	zero	0.002	Increased risk of cancer

From Fed Reg., 50:219 (November 13, 1985)

			TABLE A-2	
			Regulated VOCs under Phase II of the SDWA	
VOC	**MCLG (mg/L)**	**MCL (mg/L)**	**Sources of Drinking Water Contamination**	**Potential Health Effects**
2,4,5-TP	0.05	0.05	Herbicide on crops, right-of-ways, golf courses; canceled in 1982	Liver and kidney damage
2,4-D	0.07	0.07	Runoff from herbicide on wheat, corn, range lands, lawns	Liver and kidney damage
Acrylamide	Zero	TT	Polymers used in sewage and wastewater treatment	Cancer, nervous system effects
Alachlor	Zero	0.002	Runoff from herbicide on corn, soybeans, other crops	Cancer
Aldicarb sulfone	0.007	0.007	Biodegradation of Aldicarb	Nervous system effects
Aldicarb sulfoxide	0.007	0.007	Biodegradation of Aldicarb	Nervous system effects
Aldicarb *	0.007	0.007	Insecticide on cotton, potatoes, other crops; widely restricted	Nervous system effects
Atrazine	0.003	0.003	Runoff from use as herbicide on corn and non-crop land	Mammary gland tumors
Carbofuran	0.04	0.04	Soil fumigant on corn and cotton; restricted in some areas	Nervous, reproductivity effects
Chlordane	Zero	0.002	Leaching from soil treatment for termites	Cancer
Chlorobenzene	0.1	0.1	Waste solvent from metal degreasing processes	Nervous system and liver effects
Dibromochloro-propane (DBCP)	Zero	0.0002	Soil fumigant on soybeans, cotton, pineapple, orchards	Cancer
Dichlorobenzene o-	0.6	0.6	Paints, engine cleaning compounds, dyes, chemical wastes	Liver, kidney, blood cell damage
Dichlorobenzene p-	0.075	0.075	Paints, engine cleaning compounds, dyes, chemical wastes	Anemia; liver, kidney, or spleen damage
Dichloroethylene (cis-1,2-)	0.07	0.07	Waste solvent from metal degreasing processes; biodegradation of TCE	Ammune system problems
Dichloroethylene (trans-1,2-)	0.10	0.10	Waste solvent from metal degreasing processes; biodegradation of TCE	Liver or immune system problems
Dichloropropane (1,2-)	Zero	0.005	Soil fumigant, waste industrial solvents	Liver, kidney, effects, cancer
Epichlcrohydrin	Zero	TT	Water treatment chemicals, waste epoxy resins, coatings	Cancer

TABLE A-2 (CONT.) Regulated VOCs under Phase II of the SDWA				
VOC	**MCLG (mg/L)**	**MCL (mg/L)**	**Sources of Drinking Water Contamination**	**Potential Health Effects**
Ethyl benzene	0.7	0.7	Gasoline, insecticides, chemical manufacturing wastes	Liver, kidney, nervous system effects
Styrene	0.1	0.1	Plastics, rubber, resin, and drug industries; leachate from city landfills	Liver, nervous system damage
Toluene	1	1	Gasoline additive, manufacturing and solvent operations	Liver, kidney, nervous system and circulatory system effects
Xylenes	10	10	By product of gasoline refining, plants, inks, detergents	Liver, kidney, nervous system effects
From Pontius, Frederick "New Horizons in Federal Regulation" *Jour. AWWA,* 90(3)):38 (March 1998)				

TABLE A-3 Regulated VOCs under Phase V of the SDWA				
VOC	**MCLG (mg/L)**	**MCL (mg/L)**	**Sources of Drinking Water Contamination**	**Potential Health Effects**
Dichloromethane	Zero	0.005	Paint striper, metal degreaser, propellant, extracting	Cancer
Trichlorobenzene (1,2,4-)	0.07	0.07	Herbicide production, dye carrier	Liver, kidney damage
Trichloroethane (1,1,2,-)	0.003	0.005	Solvent in rubber, other organic products; chemical production wastes	Kidney, liver, nervous system damage

From Pontius, Frederick "New Horizons in Federal Regulation" *Jour. AWWA,* 90(3)):38 (March 1998)

APPENDIX B - VOCS PROPOSED FOR REGULATION

TABLE B-1 Proposed VOCs for Regulation						
VOC	**Regulatory Status.**	**MCLG (mg/L)**	**MCL (mg/L)**	**Status HA[1]**	**RfD[2] (mg/kg/day)**	**DWEL[3] (mg/L)**
bis-2-Chloroisopropyl ether	- -	- -	- -	Final	0.04	1
Bromobenzene	Listed[4]	- -	- -	Draft	- -	- -
Bromochloromethane	- -	- -	- -	Final	0.013	0.05
Bromodichloromethane (THM)	Proposed[5]	zero	0.1*/0.08*	Draft	0.02	0.7
Bromoform (THM)	Proposed	zero	0.1*/0.08*	Draft	0.02	0.7
Bromomethane	- -	- -	- -	Final	0.001	0.05
Chloral hydrate	Proposed	0.04	0.06	Draft	0.0002	0.06
Chlorodibromomethane (THM)	Proposed	0.06	0.1*/0.08*	Draft	0.02	0.7
Chloroethane	Listed	- -	- -	Draft	- -	- -
Chloroform (THM)	Proposed	zero	0.1*/0.08*	Draft	0.01	0.4
Chloromethane	Listed	- -	- -	Final	0.004	0.1
Chlorotoluene o-	Listed	- -	- -	Final	0.02	0.7
Chlorotoluene p-	Listed	- -	- -	Final	0.02	0.7

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[1] Health Advisory

[2] Reference Dose - an estimate of a daily exposure to the human population that is likely to be without appreciable risk of deleterious effects over a lifetime.

[3] Drinking Water Equivalent Level - a lifetime exposure concentration protective of adverse, non-cancer health effects that assumes all of the exposure to a contaminant is from a drinking water source.

[4] The compound is being considered for regulation, but a regulation has not yet been proposed.

[5] A proposed regulation that has been published by the EPA.

* The MCL applies to the sum of the following four trihalomethanes: chloroform, bromodichloromethane, chlorodibromomethane, and bromoform.